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Description

BACKGROUND OF THE INVENTION

This invention relates to a rewritable optical recording medium that can optically record, reproduce and erase information by electromagnetic energy such as light and heat, and to methods for recording and reproducing information on the optical recording medium and for recording, reproducing and erasing recorded information on the optical recording medium. Furthermore, the present invention relates to an article utilizing the properties of the optical recording medium.

Recently, research and development have been vigorously made on information recording media capable of recording information at desired parts at a high density and a high speed, and optical recording media capable of recording and reproducing information by irradiation of laser beam spot and erasing the recorded information and rewriting new information by the laser beam have been proposed.

The conventional optical recording media can be classified into various types such as a pit-forming type, a bubble or uneven surface-forming type, a photomagnetic type, a phase change type, etc. on the basis of what physical change is brought to the medium when heated by a laser beam spot, 1.5 μm in diameter, as disclosed in Nikkei Electronics January 4 issue (1982), page 86 et seq. under the title "Optical disk memory that has been just used in image files".

Among these types, only optical recording media of phase change type are rewritable. So far proposed optical recording media of phase change type are those having a thin film comprising a composition containing a chalcogenide based material or a lower oxide (Japanese Patent Publication No. 47-26897).

The optical recording media of phase change type include those based on a phase change between the amorphous state and the crystalline state or between one crystalline state and another crystalline state. Chalcognide-based substances mainly belong to the phase change type between the amorphous state and the crystalline state and include those disclosed in the Japanese Patent Publication No. 47-26897 and tellurium compounds, etc. disclosed in Japanese Patent Application Kokai (Laid-open) No. 60-253034. Cu-Al-Ni alloy or In-Sb alloy disclosed in Japanese Patent Application Kokai (Laid-open) No. 60-46339 belong to the phase change type between the crystalline states. In these optical recording media, recording and erasing are carried out by reversibly changing the structural state from one to another or vice versa. In those media of phase change type between the amorphous state and the crystalline state, recording and erasing are carried out by using the amorphous state for a recording state and the crystalline state for an unrecording state.

One of the important requirements for an optical recording medium is higher speed recording and erasing.

Conventional, rewritable optical recording media of phase change type, including those of phase change type between the amorphous state and the crystalline state and those of phase change type between one crystalline state and another crystalline state have such a problem as low speed erasing.

EP-A-212 336 and EP-A-239 166 describe some recording layers switchable between crystalline and amorphous states, made of three-component compounds, including some In Sb Te compounds.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a rewritable optical recording medium of phase change type between an amorphous and a crystalline state, which is capable of recording and erasing information at a high speed.

According to the present invention, there is provided a recording medium as set out in claim 1.

Within the present invention for example high speed recording and erasing has been actually attained by an optical recording medium comprising a recording layer whose crystalline state is composed of a single phase of a four-component compound.

The four-component compound herein referred to means a compound having a crystal structure directly determined from the Bragg's diffraction angle in the X-ray diffraction.

In the present optical recording medium, the crystalline state of the recording medium may not always be composed only of a single phase entirely of one of the kinds (i), (ii) and (iii) of claim 1.

That is, the crystalline state may be composed of a single phase mainly of one of the kinds (i), (ii) and (iii) of claim 1.

The recording layer can be formed from a raw-material composed of a mixture of components that can form the desired material by any thin film-forming means such as sputtering, vapor deposition, coating, plating, etc. When the mixture of components as the raw material is deviated from a composition capable of

forming the desired material, a single phase containing the deviated component or components is formed, but is, of course, practically applicable. Usually, the single phase must contain at least 90% by atom of the material specified at (i), (ii) and (iii) of claim 1. That is, the amount of such material must not be less than 90% by atom in the single phase.

The recording layer can contain other components than those which form the material specified at (i), (ii) and (iii) of claim 1, within such a range that the crystal structure of the single phase of the material can be maintained. The crystallization temperature and the melting temperature of the compound can be controlled and the sensitivity of recording and erasing can be increased thereby. Thus, in the case of the single phase of a three-component compound In_3SbTe_2, the melting point of the three component compound can be lowered and the sensitivity of recording and erasing can be further increased by adding at least one of silver (Ag), tin (Sn) and copper (Cu) thereto. In the case of In_3SbTe_2, the total content of silver, tin and copper is not more than 5% by atom. So long as the total content of silver, tin and copper is not more than 5% by atom, these additive components can undergo solid solution in the crystals, maintaining the crystalline state of the single phase of the three-component compound. However, when the content of silver, tin and copper increases and exceeds 10% by atom in total, another compound will be formed, resulting in phase separation and losing the single phase.

The present invention will be described in detail below, referring to the drawings.

BRIEF DESCRIPTION OF THE INVENTION

Figs. 1 to 6 are schematic cross-sectional views showing the structures of the present optical recording media.

Fig. 7 is a schematic cross-sectional view in part of an optical card according to one embodiment of the present invention.

Figs. 8a and 8b are optical characteristic diagrams of In_3SbTe_2.

Fig. 9 is a characteristic diagram showing changes in reflectivity by heating In_3SbTe_2.

Fig. 10 is a characteristic diagram showing a relationship between the reflectivity ratio and the laser output of an optical recording medium containing an In-Te-Sb film.

Figs. 11a and 11b are characteristics diagrams showing test results of repetitions of recording and erasing of an optical recording medium containing an In-Te-Sb film.

Fig. 12 is a characteristic diagram of an optical recording medium having an In-Te-Sb film.

Fig. 13 is a characteristic diagram showing differences in recording characteristics due to differences in materials of recording layer.

Fig. 14 is a characteristic diagram showing a relationship between the number of repetitions of recording and erasing and the contrast.

Fig. 15 is a characteristic diagram showing a relationship between the number of repetitions of recording and erasing and the average crystal grain size of the recording layer.

Fig. 16 is an optical characteristic diagram of $Bi_{40}Se_{20}Te_{40}$.

Fig. 17 is a characteristic diagram showing changes in reflectivity by heating $Bi_{40}Se_{20}Te_{40}$.

Fig. 18 is a characteristic diagram showing a relationship between the wavelength and the light transmissivity of optical recording media having a crystalline state of a single phase of a four-component compound.

Fig. 19 is a characteristic diagram showing a relationship between the wavelength and the spectroreflectivity of optical recording media having a crystalline state of a single phase of a four-component compound.

Fig. 20 is a characteristic diagram showing a relationship between the reflectivity ratio and the pulse width of optical recording media having a recording layer of $CuZn_2InTe_4$ and $CuInTe_2$, respectively.

Fig. 21 is a characteristic diagram showing a relationship between the erasing pulse width and the crystallization temperature.

Figs. 22(a) and 22(b) are characteristic diagrams showing a relationship between the number of repetitions of recording and erasing and the reflectivity of an optical recording medium containing $CuZn_2InTe_4$.

DETAILED DESCRIPTION OF THE INVENTION

(a) Structure of an optical recording medium:

The present optical recording medium is in a structure which comprises a substrate and a recording layer formed thereon. The substrate for use in the present invention includes a glass substrate, a metal substrate such as an aluminum substrate, an organic resin substrate such as those of polycarbonate, polymethylmethacrylate, etc.

Fig. 1 shows one embodiment of the present optical recording medium, where a recording layer 1 is provided on a substrate 2. The recording layer 1 has a thickness of preferably 50 to 200 nm and an influence of heat conduction can be disregarded in this range at the phase change. An electromagnetic energy can be applied to the medium from either substrate side or recording layer side.

Fig. 2 shows that a surface protective layer 3 is further provided on the recording layer 1. For the surface protective layer 3, ceramics with a good corrosion resistance or a good wear resistance are desirably used. The thickness of the surface protective layer 3 is desirably 100 to 500 nm, particularly 100 to 200 nm. Suitable ceramics for the surface protective layer include inorganic oxides such as SiO_2, Al_2O_3, Ta_2O_5, ZrO_2, etc., nitrides such as Si_3N_4, TaN, ZrN, AlN, TiN, etc., and fluorides such as SiF, etc.

Fig. 3 shows that a heat shielding layer 4 is provided between the substrate 2 and the recording layer 1. The heat shielding layer 4 is effective when the substrate material is an organic resin. As the material for the heat shielding layer 4, the same material as that for the surface protective layer can be used. The thickness in a range of 100 to 200 nm is quite effective for the heat shielding.

Fig. 4 shows such a structure that the recording layer 1 is sandwiched between the substrate 2 and a glass plate 5. The surface precision of the recording layer 1 can be improved to give a flat surface with much less unevenness thereby.

Fig. 5 shows that a recess is provided on the surface of the substrate 2 and the recording layer 1 is provided over the recess. The space 6 formed between the substrate 2 and the recording layer 1 is filled with air. Since the air is of very poor heat conductivity, transmission of the heat through the substrate 2 can be made smaller by the air when an electromagnetic energy spot is focused onto the recording layer. That is, the desired part of the recording layer can be locally heated thereby to undergo a phase change and much accelerate the recording speed and the erasing speed. In the structure as shown in Fig. 5, the electromagnetic energy must be applied to the recording layer 1 from the overhead of the glass plate 5.

Fig. 6 shows that a pair of substrates 2 each provided with a recording layer 1 on one side are brought into contact through a heat shielding layer 4 to make the recording layers 1 face each other, where the substrates 2 are preferably transparent glass substrates to make possible recording from both sides.

(b) Methods for recording, reproduction and erasing:

In the present invention, information can be recorded by locally focusing an electromagnetic energy to the desired part of the recording layer to make the electromagnetic energy-focused part undergo a phase change. Recording can be made by using any of the amorphous state and the crystalline state. That is, recording is made by using one of the amorphous state and the crystalline state and erasing is made by using the other state.

According to a specific embodiment of the present invention, high speed recording and high speed erasing can be made by using the amorphous state for recording and by using the crystalline state for erasing. That is, desirably recording is made by focusing an electromagnetic energy spot onto the recording layer in the crystalline state, thereby phase changing the crystalline state into the amorphous state, whereas erasing is made by phase changing the amorphous state into the crystalline state, thereby returning the recorded state to the original unrecorded state.

Reproduction can be made by detecting the state of the parts recorded by the phase change. Actually, reproduction can be carried out as optical changes.

The optical properties of the recording layer of the present optical recording medium are locally changed by a phase change. For example, reflectivity, transmissivity, absorbance, emissivity, magnetic Kerr effect, etc. are changed by a phase change. Thus, information can be reproduced by detecting any one of these optical properties.

As the electromagnetic energy, photo energy, electron energy, etc. can be utilized. The photo energy includes a laser beam, a xenon lamp, etc.

(c) Application:

The present optical recording medium can be used as an optical disk by providing a recording layer on a disk with tracking grooves, and also as an optical card or as a digital tape for audio appliances.

The optical card can be provided by forming a recording layer on the tracking grooves-provided surface of a substrate. Fig. 7 shows a preferable structure of the optical card, where a heat shielding layer 4 is formed on a substrate 2 and a recording layer 1 is formed on the heat shielding layer 4. The surface of the recording layer 1 is protected by a surface protective layer 3.

The audiodigital tape can be provided by forming a recording layer on the tracking grooves-provided surface of a flexible organic resin tape. The surface of the recording surface is desirably further protected with a protective layer.

Other requirements for an optical recording medium than the high speed recording and high speed erasing are a high resistance to moisture and oxidation, a high productivity, a high S/N ratio, etc. Furthermore, it is required that after repetitions of the phase change between the amorphous state and the crystalline state the same amorphous state and crystalline state can be always obtained and that these states will not change even after the optical recording medium is left in these states for a long time. The last requirement is very important for the rewritable optical recording medium.

The conventional optical recording medium of phase exchange type between the amorphous state and the crystalline state or between one crystalline state and another crystalline state is not satisfactory in the erasing speed. For example, a chalcogenide based material actually has a recording speed of actual level such as 0.2 μs, whereas its erasing speed is very low, for example, 5 μs.

Furthermore, the Te-based recording material has such a problem that it is readily oxidized with the moisture in the air.

The present optical recording medium has not only high recording speed and erasing speed, but also other properties of high level.

The function of the present invention will be described in detail below, referring to a recording layer whose cristalline state is of a single phase of three-component compound.

Function

Thermodynamic phase rule can be given by the following equation under a constant pressure, for example, the atmospheric pressure:

$$f = C - p + 1$$

where C stands for the number of components, p the number of phases and f the degrees of freedom.

In a single phase of a three-component compound, $C = 3$ and $p = 1$, and thus the degrees of freedom $f = 3$. Likewise, in a single phase of a two-component compound, $f = 2$. The degrees of freedom f is the numbers of variable thermodynamic quantity. For example, a single phase of three-component compound has two degrees of freedom besides the temperature. In other words, a single phase of three-component compound has one more degree of freedom for the composition than a single phase of two-component compound. This means that the three-component compound has less occurrence of phase separation (multi-phase formatoin) against changes in the single phase composition, as compared with the two-component compound. Thus, in the formation of a recording layer by vapor deposition or sputtering, the desired composition has been so far prepared by high level composition control, whereas in a single phase composition of three-component compound the single phase composition can be more readily prepared. This is effective for considerably increasing the productivity of optical recording medium, and also effective for local changes in the composition which occur at the repetitions of recording and erasing. Thus, the single phase can be maintained and the recording and erasing characteristics can be stabilized, resulting in an increase in the reliability. Furthermore, repetitions of recording and erasing can be carried out stably, resulting in an increase in the number of the repetitions. The crystallization from an amorphous state often involves complicated processes, e.g. nucleation, phase separation, structural relaxation, etc. The structural change due to the phase separation requires a long distance diffusion of atoms and thus the structure having a longer diffusion distance and a low diffusion rate (diffusion constant) has a lower crystalline rate. Nucleation of a plurality of phases (multi-phase) having considerably different crystal structures due to the phase separation requires a very long time owing to boundary strains. However, the long distance diffusion can be avoided by making a single crystallization phase and the crystallization can be highly accelerated by shorter distance diffusion in the order of band length. Furthermore, since the crystallization proceeds in the

same crystal structure, the strains become smaller and the nucleation can be also facilitated. Owing to the foregoing physical factors, the erasing speed of the optical recording medium comprising a recording layer of single phase is higher than that of the conventional recording medium based on the phase separation.

The phase change between the amorphous state and the crystalline state in a single phase has a less volume change than the phase separation in a multi-phase. In the multi-phase, the crystalline state involve an excess volume owing to the misfit states between one phase and another phase, whereas in a single phase there is no misfit state. In other words, the material has a less fatigue due to the volume change that occurs at repetitions of recording and erasing, and the single phase has an improved repetition characteristic than the plurality of phases.

The crystalline state (erasing) in the single phase has a less strain energy at the crystal grain boundary, as described before, but those in the multi-phase have a very large strain energy. The strain energy at the grain boundary can be measured as a grain boundary energy. According to the teaching of crystal grain growth rate in the metallurgy, the crystal grain growth rate dD/dt has a relationship with boundary energy γ, given by the following equation:

$$\frac{dD}{dt} = k \cdot \frac{\gamma}{D}$$

where D is an average diameter of crystal grains and k a constant.

Thus, the crystal grain growth rate will be higher with increasing grain boundary energy γ. That is, the crystal grain growth is larger when the grain boundaries are composed of a multi-phase and is smaller when composed of a single phase. This means that the single crystal phase has less crystal grain growth and consequent less reduction in the S/N ratio due to the heat cycles of recording and erasing.

As described above, the conventional recording layer materials are in a mixture of phases containing additive elements without any consideration of stoichiometry of a compound only to improve their characteristics, and thus the chemical bond correlations among the atoms therselves are indefinite in such a mixture of phases. The present invention provides an optical recording medium having a recording layer composed of a chemically stoichiometric compound, based on the finding that such a mixture of phases (multi-phase) does not improve the overall characteristics of an optical recording medium. Generally, a chalcogenide-based compound is a covalent bond solid. The covalent bond solid herein referred to is a solid, where the bonds of atoms themselves are mostly of the covalent bond type, and quantitively a solid whose covalent bond degree α_c, for example, by LCAO method (or local atomic orbital method) is 0.5 or more (W.A. Harrison: Electronic Structure and Physical Properties of Solids, translated by Tadanobu Kojima, Kazuko Kojima and Eizaburo Yamada and published by Gendai Kogaku-sha, Japan, page 117). The resistance to moisture and oxidation of a recording layer can be considerably improved by making the recording layer from a covalent bond solid of three-component compound. The solid of three-component compound is a chemically stoichiometric composition or is very approximate thereto, and thus is saturated with the covalent bonds and the excess valence electron density is so small that no bonds are formed between the oxygen atoms or between the water molecules from the outside, that is, the slid undergoes neither oxidation nor hydration (hydroxidation). Further, the stoichiometric compound is generally thermodynamically highly stable and thus undergoes no oxidation or hydration-decomposition with the result of less liberation of toxic single elements.

It can be seen from the foregoing that an optical recording medium whose recording layer is composed of a suitable single phase of three-component compound at erasing can effectively overcome the problems of the conventional materials for the recording layer owing to the physico-chemical characteristics of the recording layer composed of a single phase of three-component compound and can further improve the characteristics of the optical recording medium. It has been found that the physico-chemical characteristics of a recording layer composed of a single phase of three-component compound do not improve the characteristics of the optical recording medium as independent factors, but act integrally to bring about a synergistic effect. The present invention is also applicable to a recording layer composed of a single phase of four-component compound or higher multi-component compound.

The three-component compounds for use in the present invention are In_3SbTe_2, $AgSbTe_2$, $(AuSb)_2Te_3$, Bi_2SeTe_2, and Sb_2SnTe_4.

A four-component compound for use in the single phase in the recording layer includes, for example, $(Cu,Hg)_{12}Sb_4Se_{13}$, $(Ni,Pd)_2SbTe$, $Pd(Sb,Bi)Te$, $CuPbBiSe_3$, $CuCd_2GaSe_4$, $(Cu,Ga)CdSe_2$, $CuCd_2InSe_4$, $CuAl_4InSe_8$, $CuCdSiSe_4$, $CrCuSnSe_4$, $CuCoGeSe_4$, $Cu_2CoSnSe_4$, $CuZn_2GaSe_4$, $Cu_2FeGeSe_4$, $Cu_2FeSiSe_4$, $Cu_2FeSnSe_{3.8-4}$, $Cu_2MnGeSe_4$, $CuMnSiSe_4$, $CuMnSnSe_4$, $Cu_2HgSiSe_4$, $Cu_2NiGeSe_4$, $Cu_3FeTl_2Se_4$, $Cu_3Tl_2FeSe_4$, $CuZn_2InSe_4$, $Cu_2ZnSiSe_4$, $Ga_2InAsSe_3$, $AgAl_4InSe_8$, $PbBi_2(Se,Te)_4$, $AlNa_3SiTe_4$, $CuCd_2GaTe_4$, $CuGd_2InTe_4$, $AgCd_2InTe_4$, $CuZn_2GaTe_4$, $Cu_3FeTl_2Te_4$, $CuZn_2InTe_4$, $PdBi_2(Se,Te)_4$ and

$AgInAl_4Te_8$.

Some procedures for forming compounds used in the present invention, and other analogous compounds, will now be described.

Procedure 1

In order to find the function of an optical recording medium, vapor deposition films were prepared as recording layers. The structure of the optical recording medium was as shown in Fig. 2, and a laser beam was focused on the optical recording medium from the overhead of the substrate. The substrate was quartz glass plate, a rigid glass plate or a polycarbonate (PC) resin disk, each 1.2 mm in thickness. As a protective layer, an inorganic layer of SiO_2, AlN, Ta_2O_5, TiN, Cr_2O_3, SiN, SiC, GeN, ZrO_2, TiO_2, ZnS, or SiC was formed on the recording layer by RF sputtering. The thickness of the protective layer was 100 to 500 nm, depending upon the interference conditions of the beam transmitted through the recording layer. The desired (target) compositions of the recording films composed of a single phase of three-component compounds thus prepared, which include compounds used in the present invention, are shown below: Bi_2SeTe_2, Ga_4GeSe_8, Sb_2SeTe_4, $GaGeSe_3$, Au_2SeTe, $AgGaSe_2$, $(AuSb)_2Te_3$, Ag_9GaSe_6. Ge_2SeTe, In_3SbTe_2, Bi_4GeTe_7, $AgInTe_2$, $AgTn_5Te_3$, Ag_8GeTe_6, $CuIn_5Te_8$, $CuInTe_2$, Cu_2GeTe_3, Cu_2SnTe_3, Cu_3SbSe_4 and AgInSe .

Vapor deposition procedure applicable for forming the single phase of three-component compound includes a single source vapor deposition procedure, a two-source vapor deposition procedure and a three-source vapor deposition procedure as conventional procedures, as shown in the following Table 1.

Table 1

	Vapor deposition procedure		Analytical results
	vapor source	source combination	
conventional	Single source	Single phase of three-component compound	x
	Two sources	Two-component alloy and single element	x
	Three sources	Three simple elements	x
The invention	Two sources	Two-component compound and two-component compound	o

According to the conventional simple source vapor evaporation procedure, an alloy of the desired composition is prepared in advance, and is subjected to the vapor deposition. According to the conventional two-source vapor deposition procedure, a two-component alloy is prepared in advance and is subjected to vapor deposition as one vapor source together with a simple element as another vapor source to form a single phase of three-component compound. According to the conventional three-source vapor deposition procedure, the three simple elements are subjected to vapor deposition at the same time to form a single phase of three-component compound. On the other hand, the present vapor deposition procedure is a two-source procedure as in the conventional procedure, but a remarkable difference from the conventional two-source vapor deposition procedure using a combination of a two-component alloy as one vapor source and a single element as another source is that a combination of a pair of two-component compounds is used in

the present invention. Recording layers each composed of a single phase of the desired three-component compound as listed above were prepared according to the individual vapor deposition procedures and analyzed. The results of analysis are also shown in Table 1, where the cross mark (x) shows a considerable deviation from the desired compound composition and the circle mark (o) shows a substantially desired compound composition. As is apparent from Table 1, all the conventional procedures had the cross mark (x), whereas the present procedure had a good result. This is because the vapor deposition rate is hard to control in the conventional procedures owing to different vapor pressure of the individual elements in the single phase of three-component compound composition. Particularly, selenium and tellurium have unstable vapor deposition rates and the vapor deposition must be repeated more than 10 times to obtain the desired compound composition, and this is a serious problem in the productivity. In the present vapor deposition procedure, on the other hand, the vapor-sources are compounds themselves, which are very stable and have a larger bounding force. Thus, the desired compound composition can be obtained by one vapor deposition and the productivity is incomparably higher than that of the conventional procedures.

Procedure 2

Table 2 shows analytical results of films prepared as a recording layer from a single phase, three-component compound, $CuInTe_2$, according to the conventional vapor deposition procedures and the present vapor deposition procedure.

Table 2

$CuInTe_2$ ($Cu_{25}In_{25}Te_{50}$ % by atom)

	Vapor deposition procedure		Analysis (% by atom)		
	Vapor source	Vapor source materials	Cu	In	Te
Conventional	Single source	$Cu_{25}In_{25}Te_{50}$	5.2	10.2	84.6
	Two sources	CuIn : Te = 1 : 1	7.0	14.5	78.5
	Three sources	Cu : In : Te = 1 : 1 : 2	9.8	8.0	82.2
The invention	Two sources	InTe : CuTe = 1 : 1	23.2	26.4	50.4

$Cu_{25}In_{25}Te_{50}$ (in % by atom) as a vapor source matirial for the conventional single source vapor deposition procedure was melted and alloyed in a Siliconit furnace and used as the vapor source. In the case of the conventional two-source vapor deposition procedure, $Cu_{50}In_{50}$ was melted and alloyed in the Siliconit furnace and used together with Te as vapor sources, where vapor deposition rates of $Cu_{50}In_{50}$ and Te were measured, respectively, in advance and vapor deposition was carried out in a ratio of CuIn : Te = 1 : 1. In the case of the conventional three-source vapor deposition procedure, three elements, Cu, In and Te, were used, where vapor deposition rates of Cu, In and Te were measured, respectively, in advance and vapor deposition was carried out in an ratio of Cu : In : Te = 1 : 1 : 2. In the present invention, on the other hand, two-component compounds, InTe and CuTe, were melted and alloyed in the Siliconit furnace, respectively, and then pulverized. The thus obtained two powdery compounds were used as vapor sources to form a film composed of a single pahse of three-component compound.

The individual vapor sources were placed on tungsten or molybdenum boats in a vapor deposition chamber, respectively, and the vapor deposition chamber was evacuated to a vacuum degree of 5×10^{-6} Torr and then the vapor sources were subjected to vapor deposition each to form a vapor deposition film on a substrate to a film thickness of 80 to 120 nm. The thus obtained films were subjected to ICP analysis. As is apparent from the analytical results of Table 2, no desired compositions were obtained in the conventional procedures, whereas the film obtained by simultaneous vapor deposition of the two-component compounds, InTe and CuTe, according to the present invention had a substantially desired composition.

As a vapor deposition chamber for the present invention, a two-source resistance-heating vapor deposition chamber was used.

Procedure 3 (Example of the invention)

Table 3 shows analytical results of films composed of a single phase of three-component compound, In_3SbTe_2, prepared according to the conventional vapor deposition procedures and the present vapor deposition procedure under the same preparation conditions as in Procedure 2. As is apparent from the analytical results of Table 3, the present vapor deposition procedure was distinguished in obtaining a film of desired composition, as in Procedure 2.

Table 3

In_3SbTe_2 ($In_{50}Sb_{17}Te_{33}$ in % by atom)

	Vapor deposition procedure		Analysis (% by atom)		
	Vapor source	Vapor deposition materials	In	Sb	Te
Conventional	Single source	$In_{50}Sb_{17}Te_{33}$	20.2	34.8	45.0
	Two sources	SbTe : In 1 : 1	34.5	12.5	53.0
	Three sources	In : Sb : Te 2 : 1 : 1	42.5	27.5	30.0
The invention	Two sources	InSb : InTe 1 : 2	48.2	16.5	35.3

Optical characteristics of In_3SbTe_2 are shown in Figs. 8a and 8b. Fig. 8a shows spectroscopic characteristics of an optical recording medium having a film prepared in the same manner as above as a recording layer and a protective film of SiO_2 having a thickness of 100 nm, formed on the recording layer. Fig. 8b shows spectroscopic characteristics of the same optical recording medium as above, heated up to 350 °C, that temperature for 5 minutes and then slowly cooled. At the semiconductor laser wavelength of 830 nm, the reflectivity was increased to 40% from 34% and the transmissivity was decreased to 1% from 8% by the heat treatment. This shows that the optical characteristics were greatly changed by a phase change from the amorphous state to the crystalline state.

Fig. 9 shows measurement results of dynamic change in the reflectivity by heating, where the reflectivity abruptly increased at 188 °C. This shows that the present optical recording medium can undergo high speed erasing. The film prepared according to the present vapor deposition procedure had a analytical composition of $In_{51}Sb_{17}Te_{32}$ (in % by atom) and it seems that a single phase of three-component

compound, In_3SbTe_2, was formed. According to the phase diagram of pseudo-binary system of InTe-InSb, the melting point at a metastable state of In_3SbTe_2 is 568 °C and the single phase dominates just up to the melting point. Thus, at the recording, an amorphous state can be obtained by heating to higher than the single melting point, followed by quenching. Since the melting point of a single phase compound is substantially single, the single phase compound will melt at a definite temperature at that time, and thus the high speed recording can be made. Furthermore, since the single phase of three-component compound can dominate against heating just up to the melting point, a phase change from the amorphous state to the crystalline state can be made at the erasing by heating just up to the melting point from the crystallization temperature without phase separation. Since the crystallization is 188 °C, as seen from Fig. 9, superheating by 380 °C can be obtained. The absence of phase separation unnecessitates a long distance diffusion and thus high speed erasing can be made.

Procedure 4 (Example of the invention)

An In-Te-Sb film was formed on a transparent glass substrate or a polycarbonate substrate to a film thickness of 100 mm by DC magnetron sputtering. The sputtering target was prepared by melting in an Ar atmosphere. The sputtering conditions were an output power of 100 W, an initial vacuum degree of 8.5 x 10^{-5} Pa, an Ar partial pressure of 20 m Torr with water cooling of the substrate. The thus formed In-Te-Sb film was found by analysis to have a composition of $In_{49}Sb_{20}Te_{31}$ (in % by atom), which was substantially identical with the composition of the compound obtained by vapor deposition. Thus, the spectroscopic characteristics and crystallization temperature were substantially identical with those of the vapor deposited film, and the same reproducibility as that of the vapor deposited film was obtained.

Fig. 10 shows recording and erasing characteristics of an optical recording medium having the sputtering film prepared in the same manner as above as a recording layer and a SiO_2 film having a thickness of 100 nm, formed in the same manner as in Example 1, where the initial state is an amorphous state and the reflectivity ratio increases by increasing the laser output power from 2 mW to 4 mW and further to 6 mW. This increase in the reflectivity ratio means a contribution to a phase change from the amorphous state to the crystalline state. With further increase of the laser output power to 7 mW or higher, the recording is initiated, and the reflectivity ratio starts to decrease.

Figs. 11a and 11b show results of repetitions of recording and erasing of the present recording medium, that is, the results obtained by repeating recording and erasing 10 times as the initialization, thereby stabilizing the optical recording medium and then by making 10^6 repetitions of recording and erasing under the recording conditions of laser output power of 13 mW and pulse width of 0.02 μm and the erasing conditions of 8 mW and and 0.03 μs, where the average contrast was 18% at the repetition test. Thus, the present optical recording medium can overwrite for 0.03 μs, that is, can erase the recorded information for 0.03 μs and record new information at the same speed. The contrast is still as small as 18% in this test, but can be increased to about 25% by optimizing the film thicknesses of the recording layer and the protective layer and the materials of the protective layer.

Fig. 12 shows a characteristic map of the present optical recording medium. The present optical recording medium can undergo high speed recording and erasing because a recording layer composed of a single phase of three-component compound is subjected to recording just above the melting point and to erasing just below the melting point. The present optical recording medium has a broad erasing region as a characteristic. There is a film breakage region, which is, however, at the long pulse side. Thus, the film breakage hardly occurs even at a high laser output power and much higher speed recording and erasing can be made with a laser of higher output power.

Further examples of optical recording media of the invention will now be described.

Example 5

Fig. 13 shows static state recording test results of optical recording media having a recording layer of In-Te-Sb system, that is, $In_{50}Sb_{15}Te_{35}$, a composition that precipitates In_3SbTe_2 in a single phase at the crystallization; $In_{17}Sb_{48}Te_{35}$, a composition that precipitate compounds in two phases; $In_{20}Sb_{15}Te_{65}$, a composition that precipitates Te in a single phase. The recording conditions were that the pulse width was gradually made longer at the laser output power of 12 mW. The initial states were just the same states as the films were formed and were each identified to be amorphous states. In all the compositions, the reflectivity increased at first by crystallization and melting started by making the pulse width larger, thereby effecting partial heating to a temperature over the melting point. That is, the recording layer was brought into a recording state, whereby the reflectivity was decreased. It was found by comparing the results of the

three compositions that the composition that precipitates the In_3SbTe in a single phase had the highest erasing and recording speeds, the composition that precipitate the compounds in two phases had the next highest speeds and the composition that precipitates Te in a single phase had the lowest speeds. That is, the single phase region of three-component compound had the best recording and erasing characteristics.

Example 6

Table 4 shows the results of durability tests of the compositions given in the Table 4 at a temperature of 40 °C and a humidity of 90% for 10 days. Test pieces were optical recording media each having a recording layer composed of one of the compositions and formed to a thickness of 100 nm on a glass substrate and a protective film of SiO_2 formed to a thickness of 100 nm on the recording layer and having been subjected to pulse recording with 12 mW and 0.5 μs.

Table 4

Crystalline phase identified by X-rays	Durability test at constant temperature of 40°C and humidity of 90% for 10 days
Single phase composition of In_3SbTe_2	No change
In_3SbTe_2 + In_3Te_3 (In_3SbTe_2 : 80%)	No change
In_2Te_3 + Te	Considerable change

The single phase composition of In_3SbTe_2 and a double phase composition of In_3SbTe_2 + In_2Te_3 (the content of In_3SbTe_2 is 80%) had no change, whereas the composition that precipitates In_2Te_3 + Te had a change in the recording layer and had a higher transmissivity and it was found by microscopic observation that its recorded signal was obscure, because it seems that Te was changed to TeO_x. So far as Te exists as a stable compound, it is saturated with divalent bonds and never undergoes oxidation even in an oxidizing atmosphere, whereas when Te is precipitated as a simple substance, it undergoes a phase change from the amorphous state to the crystalline state even at room temperature or it is oxidized to TeO_x. Thus, the recording layer is deficient in stability. In other words, it is very important to use a recording layer having a composition range that never precipitates an elemental simple substance at the crystallization.

Example 7

Figs. 14 and 15 show relationships between the contrast and the average crystal grain size when recording and erasing are repeated, where repetition characteristics of single phase, three-component composition of a three-component compound In_3SbTe_2 and two-phase, three-component composition of two-component compounds Sb_2Te_3 + In_2Te_3 are given. The single phase, three-component composition had no change in the contrast after 10^6 repetitions of recording and erasing, whereas the contrast of the two-phase, three-component composition of Sb_2Te_3 + In_2Te_3 was about 20% lowered after 10^6 repetitions.

Fig. 15 shows the average crystal grain sizes after 10^2 repetitions, 10^4 repetitions and 10^6 repetitions. The single phase, three-component composition of a three-component compound had substantially equal crystal grain sizes throughout all the repetitions, whereas the crystal grain sizes of the two-phase, three-component composition that precipitates two-component compounds in two phases had a tendency to become larger with increasing number of repetitions. This is because, when two two-component compounds having different surface energies are formed in two phases, the surface energies will be higher than at the crystal grain boundaries of the same species compounds themselves and thus a change takes place in

such a direction as to reduce the surface area. That is, the repetition characteristics of the two-phase, three-component composition that precipitates two-component compounds in two phases are not better than those of the single phase composition of three-component compound.

Example 8

The Bi-Se-Te system has a three-component compound of $Bi_{40}Se_{20}Te_{40}$. A film of the composition was formed as a recording layer on a substrate by vapor deposition. As vapor sources Bi_2Te_3 and SiSe were prepared by melting and subjected to two-source vapor deposition at an initial vacuum degree of 3×10^{-6} Torr with water cooling of the substrate to form the film. Then, a protective film of SiO_2 was formed on the recording layer to a thickness of 100 nm to obtain an optical recording medium.

Fig. 16 shows optical characteristics of the film of $Bi_{40}Se_{20}Te_{40}$ just as vapor deposited, where the reflectivity is 27.0%, the transmissivity 2.3% and the absorbance 70.7 at a wavelength of 830 nm.

Fig. 17 shows changes in the reflectivity when the optical recording medium was heated at a temperature increase rate of 20 °C/min, where the reflectivity takes a sharp rise at 118 °C, which contributes to a phase change from the amorphous state to the crystalline state. It can be seen therefrom that the crystallization takes place within a very narrow temperature range and thus the single phase composition of the three-component compound can perform high speed erasing.

Example 9

Table 5 shows analytical results of films of single phase, three-component compound, $AgSbTe_2$, prepared according to the conventional vapor deposition procedures and the present vapor deposition procedure in the same manner as in Procedure 2 above. The desired composition was not obtained according to the conventional procedures whereas the substantially satisfactory composition as desired was obtained according to the present invention.

Table 5

$AgSbTe_2$ ($Ag_{25}Sb_{25}Te_{50}$ in % by atom)

	Vapor deposition procedure		Analysis (% by stom)		
	Vapor sources	Vapor deposition materials	Ag	Sb	Te
The conventional procedure	Single source	$Ag_{25}Sb_{25}Te_{50}$	12.2	30.8	57.0
	Two sources	AgSb : Te 1 : 1	12.0	24.6	63.4
	Three sources	Ag : Sb : Te 1 : 1 : 2	42.5	22.5	35.0
The invention	Two sources	Sb_2Te_3 : Ag_2Te_2 1 : 1	23.0	24.2	52.8

Example 10

A film of $CuZn_2InT_4$ as an example of single phase, four-component compound was formed on a substrate in a DC magnetron sputtering chamber. The sputtering target was prepared by melting in an Ar atmosphere at an output power of 100 W, an initial vacuum degree of 8.5×10^{-5} Torr and an Ar partial pressure of 20 m Torr with water cooling of the substrate. This alloy film can be likewise formed also by vacuum vapor deposition.

Fig. 18 shows an example of adding Zn for improving the light absorption to $CuInTe_2$ to make $CuZn_2InTe_4$, whereby the transmissivity at a semiconductor laser wavelength of 830 nm was reduced to 9% from 18% at equal thicknesses of 100 nm, and thus the absorbance was increased. The power of semiconductor laser on the film surface on the substrate that can be output up to now is about 15 mW and thus the recording speed can be increased by efficient absorption of the laser beam with such power.

Fig. 19 shows changes in the reflectivity when an optical recording medium having a recording layer of $CuInTe_2$ and that having a recording layer of $CuZn_2InTe_4$ were heated. By adding Zn to $CuInTe_2$, the crystallization temperature due to changes in the reflectivity was increased from 200 °C to 420 °C, though the reflectivity at room temperature was substantially the same therebetween. Such a high crystallization temperature shows that the stability of amorphous state is high at room temperature.

Fig. 20 shows a reflectivity ratio when an optical recording medium having a recording layer of $CuInTe_2$ and that having a recording layer of $CuZn_2InTe_4$ were exposed to a laser pulse of 10 mW. By irradiation of short pulse onto the recording layer in an amorphous state, the crystallization took place, thereby increasing the reflectivity ratio. $CuZn_2InTe_4$ had a higher crystallization temperature than that of $CuInTe_2$, and thus was not crystallized unless irradiated with a relatively strong laser of 12 mW, but its crystallization speed was much accelerated. That is, high speed erasing was possible. Most of so far available recording layer materials can undergo erasing with a weak laser beam but the erasing speed is low. On the other hand, the present recording layer materials have a high crystallization temperature and high speed erasing can be made with a relatively strong laser beam.

Fig. 21 shows erasing pulse width obtained for recording layers having different crystallization temperatures from the results of Fig. 20, where a single phase, four-component compound having the highest crystallization temperature has the shortest erasing pulse width and thus can undergo the fastest erasing. The foregoing characteristics can be obtained with compound composition comprising 10 to 15% of Cu, 20 to 30% of Zn and 8 to 17% of In, the balance being Te and containing a single phase, four-component compound as the main component.

Figs. 22a and 22b show repetition characteristics of an optical recording medium having a recording layer of $CuZn_2InTe_4$, where distinguished repetition characteristics can be obtained owing to the single phase, 4-component compound without any fear of phase separation.

Claims

1. An optical recording medium, which comprises a recording layer (1) capable of reversibly undergoing a phase change between a crystalline state and an amorphous state by irradiation of electromagnetic energy, characterised in that the crystalline state of the recording layer (1) is composed of a single phase which is mainly or entirely one of (i) a multi-component compound of more than three components, (ii) In_3SbTe_2 containing optionally not more than 5% by weight in total of at least one of Ag, Sn and Cu and (iii) Bi_2SeTe_2, Sb_2SnTe_4, $Au_2Sb_2Te_3$ or $AgSbTe_2$.

2. An optical recording medium according to claim 1 wherein said crystalline state of the recording layer (1) is composed of a single phase which is mainly or entirely of a four-component compound.

3. An optical recording medium according to claim 2 wherein said crystalline state of the recording layer (1) is composed of a single phase which is a four-component compound.

4. An optical recording medium according to claim 1 or claim 2 wherein said crystalline state of the recording layer (1) is composed of a single phase which is at least 90% by atom of (i) said multi-component compound of more than three components, (ii) In_3SbTe_2 and optionally not more than 5% by weight in total of at least one of Ag, Sn and Cu or (iii) Bi_2SeTe_2, Sb_2SnTe_4, $Au_2Sb_2Te_3$ or $AsSbTe_2$.

5. An optical recording medium according to claim 1 wherein said crystalline state of the recording layer (1) is composed of a single phase consisting of In_3SbTe_2 and not more than 5% by weight in total of at

least one of Ag, Sn and Cu.

6. An optical recording medium according to any one of claims 1 to 5 having on the recording layer (1) a surface protective layer (3) composed of at least one of an inorganic oxide, an inorganic nitride and an inorganic fluoride.

7. An optical recording medium according to claim 6, wherein the surface protective layer (3) is a glass plate.

8. An optical recording medium according to any one of claims 1 to 7 which comprises an organic resin substrate (2) for said recording layer (1) and a heat shielding layer (4) provided between the recording layer (1) and the substrate.

9. An optical recording medium according to any one of claims 1 to 5 which comprises a pair of glass substrates (2) each carrying a said recording layer (1) capable of reversibly undergoing a phase change between a crystalline state and an amorphous state, the recording layers (1) on the respective glass substrates (2) being opposed to each other face to face through a heat shielding layer (4) provided between them.

10. An optical recording medium according to any one of claims 1 to 6 which comprises a substrate (2) for said recording layer (1) and an enclosed recess (6) filled with air on the surface of the substrate (2) in contact with the recording layer (1).

11. A method for optical recording and reproduction, using a recording medium according to any one of claims 1 to 10, which comprises:

locally applying electromagnetic energy to a part of the recording layer (1) of said recording medium to cause the part to undergo a phase change, thereby recording information; and

detecting the state of the phase-changed part, thereby reproducing the information recorded on the phase-changed part.

12. A method according to claim 11 wherein said applied electromagnetic energy causes said part to change from a crystalline state into an amorphous state to record information.

13. A method according to claim 11 or claim 12 wherein the detection of the state at the phase changed part is carried out by detection of a difference in an optical property.

14. A method according to claim 13 wherein any one of reflectivity, transmissivity, absorbance, emissivity and magnetic Kerr effect is detected as the optical property.

15. A method for optical recording, reproduction and erasing using a recording medium according to any one of claims 1 to 10, which comprises:

locally applying electromagnetic energy to a part of the recording layer (1) of said recording medium to cause the part to undergo a phase change, thereby recording information;

detecting the state of the phase changed part, thereby reproducing the information recorded on the phase-changed part; and

applying electromagnetic energy to at least a portion of the phase-changed part to cause the said portion to undergo a phase change to the original state, thereby erasing the recorded information.

16. An optical recording medium according to any one of claims 1 to 6 which is an optical card which comprises a substrate having tracking grooves on a surface, said recording layer (1) being provided on said surface having tracking grooves.

17. An optical recording medium according to claim 16 having a heat shielding layer between said surface of the substrate having tracking grooves and said recording layer, and a surface protective layer on the recording layer.

18. An optical recording medium according to any one of claims 1 to 6 which is an audiodigital tape which comprises a flexible tape having tracking grooves on a surface, said recording layer (1) being provided

on said surface having tracking grooves.

19. An optical recording medium according to any one of claims 1 to 6 which comprises a disk having tracking grooves, said recording layer (1) being provided on said surface having tracking grooves.

Patentansprüche

1. Optisches Aufzeichnungsmedium, das eine Aufzeichnungsschicht (1) aufweist, die dazu in der Lage ist, einen Phasenübergang zwischen einem kristallinen Zustand und einem amorphen Zustand durch Einstrahlen elektromagnetischer Energie zu erfahren, **dadurch gekennzeichnet,** daß der kristalline Zustand der Aufzeichnungsschicht (1) aus einer einzelnen Phase besteht, die teilweise oder ganz aus folgendem besteht: (i) einer Mehrkomponentenverbindung aus mehr als drei Komponenten, (ii) In_3SbTe_2, das wahlweise nicht mehr als 5 Gew.% insgesamt von mindestens einem der Elemente Ag, Sn und Cu enthält, und (iii) Bi_2SeTe_2, Sb_2SnTe_4, $Au_2Sb_2Te_3$ oder $AgSbTe_2$.

2. Optisches Aufzeichnungsmedium nach Anspruch 1, bei dem der kristalline Zustand der Aufzeichnungsschicht (1) aus einer einzelnen Phase besteht, die hauptsächlich oder ganz eine Vierkomponentenverbindung ist.

3. Optisches Aufzeichnungsmedium nach Anspruch 2, bei dem der kristalline Zustand der Aufzeichnungsschicht (1) aus einer einzelnen Phase besteht, die eine Vierkomponentenverbindung ist.

4. Optisches Aufzeichnungsmedium nach Anspruch 1 oder Anspruch 2, bei dem der kristalline Zustand der Aufzeichnungsschicht (1) aus einer einzelnen Phase besteht, bei der mindestens 90 Atom-% aus folgendem bestehen: (i) der genannten Mehrkomponentenverbindung mit mehr als drei Komponenten, (ii) In_3SbTe_2 und wahlweise nicht mehr als 5 Gew.% insgesamt von mindestens einem der Elemente Ag, Sb und Cu, oder (iii) Bi_2SeTe_2, Sb_2SnTe_4, $Au_2Sb_2Te_3$ oder $AsSbTe_2$.

5. Optisches Aufzeichnungsmedium nach Anspruch 1, bei dem der kristalline Zustand der Aufzeichnungsschicht (1) aus einer einzelnen Phase besteht, die aus In_3SbTe_2 und nicht mehr als 5 Gew.% insgesamt mindestens eines der Elemente Ag, Sn und Cu besteht.

6. Optisches Aufzeichnungsmedium nach einem der Ansprüche 1 bis 5, das auf der Aufzeichnungsschicht (1) eine Oberflächenschutzschicht (3) aufweist, die aus mindestens einem anorganischen Oxid, einem anorganischen Nitrid und einem anorganischen Fluorid besteht.

7. Optisches Aufzeichnungsmedium nach Anspruch 6, bei dem die Oberflächenschicht (3) eine Glasplatte ist.

8. Optisches Aufzeichnungsmedium nach einem der Ansprüche 1 bis 7, das ein Kunststoffsubstrat (2) für die Aufzeichnungsschicht (1) und eine Wärmeschutzschicht (4) aufweist, die zwischen der Aufzeichnungsschicht (1) und dem Substrat vorhanden ist.

9. Optisches Aufzeichnungsmedium nach einem der Ansprüche 1 bis 5, das ein Paar Glassubstrate (2) aufweist, von denen jedes eine Aufzeichnungsschicht (1) trägt, die einen reversiblen Phasenübergang zwischen einem kristallinen Zustand und einem amorphen Zustand erfahren kann, wobei die Aufzeichnungsschichten (1) auf den jeweiligen Glassubstraten (2) einander mit der dazwischenliegenden Wärmeschutzschicht (4) zugewandt sind.

10. Optisches Aufzeichnungsmedium nach einem der Ansprüche 1 bis 6, das ein Substrat (2) für die Aufzeichnungsschicht (1) und eine mit Luft gefüllte, umschlossene Aussparung (6) auf der Oberfläche des Substrates (2) in Berührung mit der Aufzeichnungsschicht (1) aufweist.

11. Verfahren zum optischen Aufzeichnen und Wiedergeben unter Verwendung eines Aufzeichnungsmediums gemäß einem der Ansprüche 1 bis 10, das folgendes aufweist:

- örtliches Anlegen elektromagnetischer Energie an einen Teil der Aufzeichnungsschicht (1) des Aufzeichnungsmediums, um zu bewirken, daß der Teil einen Phasenübergang erfährt, wodurch Information aufgezeichnet wird; und

- Erfassen des Zustandes des Teils mit dem Phasenübergang, wodurch die auf dem Teil mit dem Phasenübergang aufgezeichnete Information wiedergegeben wird.

12. Verfahren nach Anspruch 11, bei dem die angelegte elektromagnetische Energie bewirkt, daß der genannte Teil von einem kristallinen Zustand in einen amorphen Zustand übergeht, um Information aufzuzeichnen.

13. Verfahren nach Anspruch 11 oder Anspruch 12, bei dem das Erfassen des Zustandes im Teil mit dem Phasenübergang dadurch ausgeführt wird, daß ein Unterschied einer optischen Eigenschaft erfaßt wird.

14. Verfahren nach Anspruch 13, bei dem das Reflexionsvermögen, das Transmissionsvermögen, das Absorptionsvermögen, das Emissionsvermögen oder der magnetische Kerreffekt als optische Eigenschaft erfaßt wird.

15. Verfahren zur optischen Aufzeichnung, Wiedergabe und Löschung unter Verwendung eines Aufzeichnungsmediums gemäß einem der Ansprüche 1 bis 10, das folgendes aufweist:

- örtliches Anlegen elektromagnetischer Energie an einen Teil der Aufzeichnungsschicht (1) des Aufzeichnungsmediums, um zu bewirken, daß der Teil einen Phasenübergang erfährt, wodurch Information aufgezeichnet wird; und
- Erfassen des Zustandes des Teils mit dem Phasenübergang, wodurch die auf dem Teil mit dem Phasenübergang aufgezeichnete Information wiedergegeben wird; und
- Anlegen elektromagnetischer Energie an mindestens einen Abschnitt des Teils mit dem Phasenübergang, um zu bewirken, daß dieser Abschnitt einen Phasenübergang in den Ursprünglichen Zustand erfährt, wodurch die aufgezeichnete Information gelöscht wird.

16. Optisches Aufzeichnungsmedium nach einem der Ansprüche 1 bis 6, das eine optische Karte ist, die ein Substrat mit Spurführungsnuten auf einer Oberfläche aufweist, wobei die Aufzeichnungsschicht (1) auf der Oberfläche mit den Spurführungsnuten vorhanden ist.

17. Optisches Aufzeichnungsmedium nach Anspruch 16 mit einer Wärmeschutzschicht zwischen der Oberfläche des Substrats mit den Spurführungsnuten und der Aufzeichnungsschicht, und einer Oberflächenschutzschicht auf der Aufzeichnungsschicht.

18. Optisches Aufzeichnungsmedium nach einem der Ansprüche 1 bis 6, das ein digitales Audioband mit einem flexiblen Band mit Spurführungsnuten auf einer Oberfläche ist, wobei die Aufzeichnungsschicht (1) auf der Oberfläche mit den Spurführungsnuten vorhanden ist.

19. Optisches Aufzeichnungsmedium nach einem der Ansprüche 1 bis 6, das eine Platte mit Spurführungsnuten aufweist, wobei die Aufzeichnungsschicht (1) auf der Oberfläche mit den Spurführungsnuten vorhanden ist.

Revendications

1. Support d'enregistrement optique, qui comprend une couche d'enregistrement (1) apte à être, de façon réversible, le siège d'un changement de phase entre un état cristallin et un état amorphe sous l'effet d'une irradiation par une énergie électromagnétique, caractérisé en ce que l'état cristallin de la couche d'enregistrement est constitué par une seule phase, qui est constituée principalement ou entièrement par l'un de (i) un composé à constituants multiples comprenant plus de trois constituants, (ii) In_3SbTe_2 contenant facultativement pas plus de 5 % en poids au total d'au moins l'un de Ag, Sn et Cu, et (iii) Bi_2SeTe_2, Sb_2SnTe_4, $Au_2Sb_2Te_3$ ou $AgSbTe_2$.

2. Support d'enregistrement optique selon la revendication 1, dans lequel ledit état cristallin de la couche d'enregistrement (1) est constitué par une seule phase, qui est formée principalement ou entièrement par un composé à quatre constituants.

3. Support d'enregistrement optique selon la revendication 2, dans lequel l'état cristallin de la couche d'enregistrement (1) se compose d'une seule phase, qui est un composé à quatre constituants.

4. Support d'enregistrement optique selon la revendication 1 ou 2, dans lequel ledit état cristallin de la couche d'enregistrement (1) se compose d'une seule phase, qui est formée d'au moins 90 % en atomes de(i) ledit composé à constituants multiples comprenant plus de trois constituants, (ii) In_3SbTe_2 et facultativement pas plus de 5 % en poids, au total, d'au moins l'un de Ag, Sn et Cu ou (iii) Bi_2SeTe_2, Sb_2SnTe_4, $Au_2Sb_2Te_3$ ou $AsSbTe_2$.

5. Support d'enregistrement optique selon la revendication 1, dans lequel ledit état cristallin de la couche d'enregistrement (1) se compose d'une seule phase constituée de In_3SbTe_2 et de pas plus de 5 % en poids, au total, d'au moins l'un de Ag, Sn et Cu.

6. Support d'enregistrement optique selon l'une quelconque des revendications 1 à 5, comprenant, sur la couche d'enregistrement (1), une couche superficielle protectrice (3) constituée par au moins l'un d'un oxyde minéral, d'un nitrure minéral et d'un fluorure minéral.

7. Support d'enregistrement optique selon la revendication 6, dans lequel la couche superficielle protectrice (3) est une plaque de verre.

8. Support d'enregistrement optique selon l'une quelconque des revendications 1 à 7, qui comprend un substrat (2) formé d'une résine organique pour ladite couche d'enregistrement (1) et une couche de protection thermique (4) disposée entre la couche d'enregistrement (1) et le substrat.

9. Support d'enregistrement optique selon l'une quelconque des revendications 1 à 5, qui comprend un couple de substrats en verre (2) portant chacun ladite couche d'enregistrement (1) apte à être, de façon réversible, le siège d'un changement de phase entre un état cristallin et un état amorphe, les couches d'enregistrement (1) sur les substrats en verre respectifs (2) étant disposées face à face moyennant l'interposition entre elles d'une couche de protection thermique (4).

10. Support d'enregistrement optique selon l'une quelconque des revendications 1 à 6, qui comprend un substrat (2) pour ladite couche d'enregistrement (1) et un renfoncement renfermé (6) rempli d'air, dans la surface du substrat (2) en contact avec la couche d'enregistrement (1).

11. Procédé d'enregistrement et de lecture optique, utilisant un support d'enregistrement selon l'une quelconque des revendications 1 à 10, qui comprend :

l'application locale d'une énergie électromagnétique à une partie de la couche d'enregistrement (1) dudit support d'enregistrement pour amener cette partie à subir un changement de phase, qui permet l'enregistrement d'une information; et

la détection de l'état de la partie ayant subi le changement de phase, ce qui permet la lecture de l'information enregistrée dans la partie ayant subi le changement de phase.

12. Procédé selon la revendication 11, dans lequel ladite énergie électromagnétique appliquée amène ladite partie à passer d'un état cristallin à un état amorphe pour l'enregistrement d'une information.

13. Procédé selon la revendication 11 ou 12, selon lequel la détection de l'état dans la partie ayant subi le changement de phase est exécutée par détection d'une différence d'une propriété optique.

14. Procédé selon la revendication 13, selon lequel la réflectivité, la transmissivité, l'absorbance, l'émissivité ou l'effet Kerr magnétique est détecté en tant que propriété optique.

15. Procédé pour l'enregistrement, la lecture et l'effacement optique moyennant l'utilisation d'un support d'enregistrement selon l'une quelconque des revendications 1 à 10, qui comprend :

l'application locale d'une énergie électromagnétique à une partie de la couche d'enregistrement (1) dudit support d'enregistrement pour amener cette partie à subir un changement de phase, qui permet l'enregistrement d'une information; et

la détection de l'état de la partie ayant subi le changement de phase, ce qui permet la lecture de l'information enregistrée dans la partie ayant subi le changement de phase; et

l'application d'une énergie électromagnétique à au moins une région de la partie ayant subi le changement de phase de manière à amener cette région à subir un changement de phase l'amenant dans l'état initial, ce qui permet l'effacement de l'information enregistrée.

16. Support d'enregistrement optique selon l'une quelconque des revendications 1 à 6, qui est une carte optique qui comprend un substrat comportant des rainures de suivi sur une surface, ladite couche d'enregistrement (1) étant disposée sur ladite surface comportant des rainures de suivi.

17. Support d'enregistrement optique selon la revendication 16, comportant une couche de protection thermique disposée entre ladite surface des substrats comportant des rainures de suivi, et ladite couche d'enregistrement, et une couche superficielle protectrice située sur la couche d'enregistrement.

18. Support d'enregistrement optique selon l'une quelconque des revendications 1 à 6, qui est une bande audio numérique qui comprend une bande flexible, dans une surface de laquelle sont ménagées des rainures de suivi, ladite couche d'enregistrement (1) étant disposée sur ladite surface comportant des rainures de suivi.

19. Support d'enregistrement optique selon l'une quelconque des revendications 1 à 6, qui comprend un disque possédant des rainures de suivi, ladite couche d'enregistrement (1) étant disposée sur ladite surface comportant des rainures de suivi.

FIG. 1

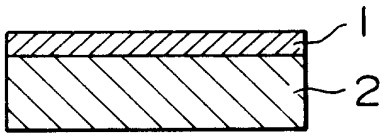


FIG. 2

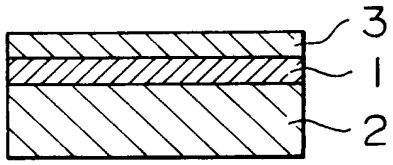


FIG. 3

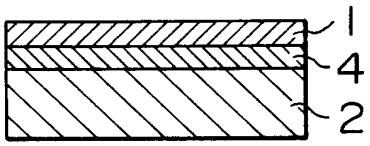


FIG. 4

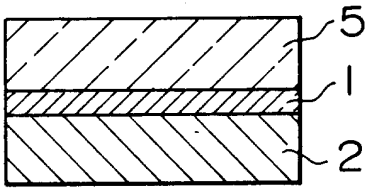


FIG. 5

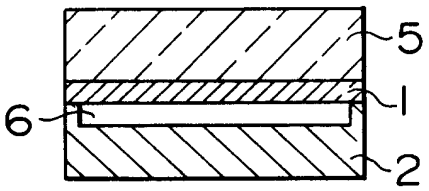


FIG. 6

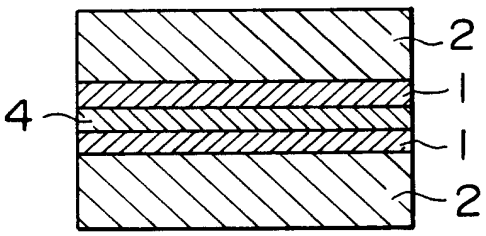


FIG. 7

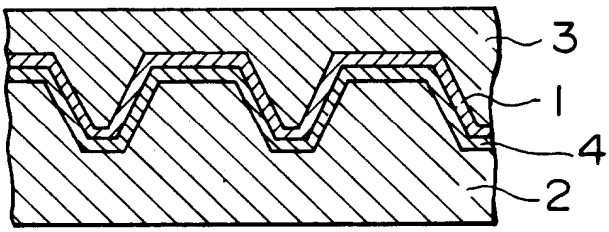


FIG. 8a

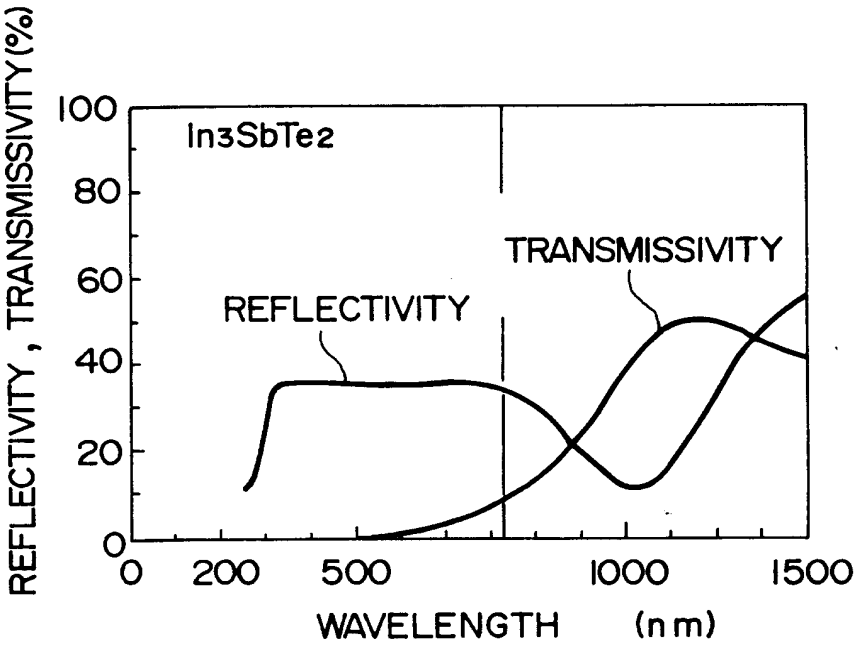

REFLECTIVITY, TRANSMISSIVITY (%)
100
80
60
40
20
0
In3SbTe2
TRANSMISSIVITY
REFLECTIVITY
0
200
500
1000
1500
WAVELENGTH (nm)

FIG. 8b

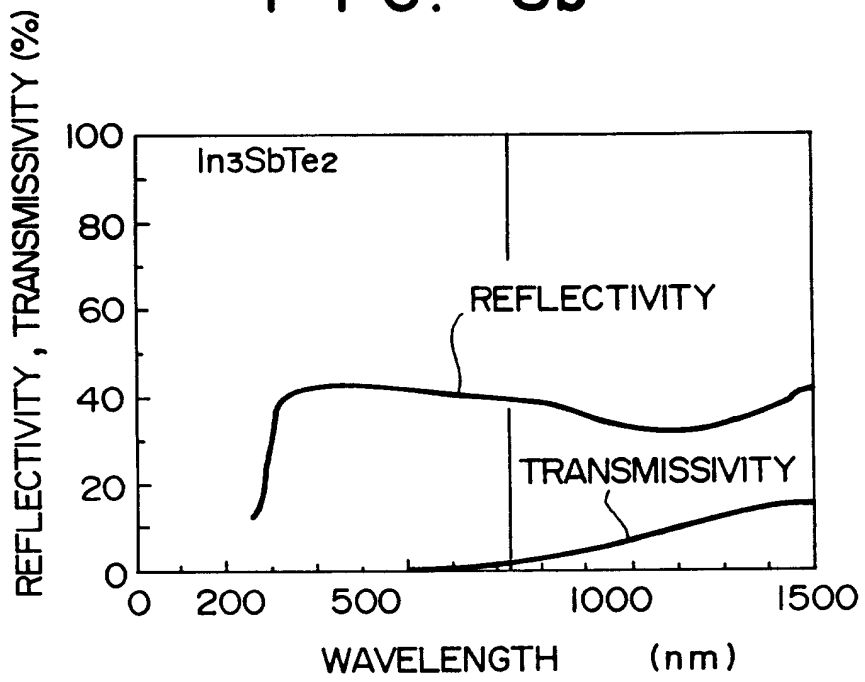

REFLECTIVITY, TRANSMISSIVITY (%)
100
80
60
40
20
0
In3SbTe2
REFLECTIVITY
TRANSMISSIVITY
0
200
500
1000
1500
WAVELENGTH (nm)

FIG. 9

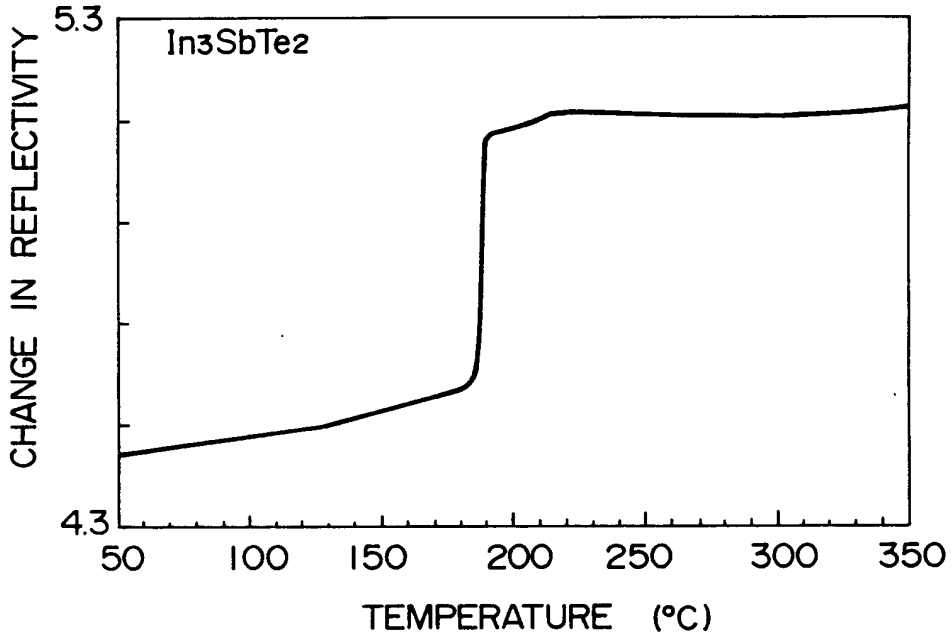

In3SbTe2
CHANGE IN REFLECTIVITY
5.3
4.3
50
100
150
200
250
300
350
TEMPERATURE (°C)

FIG. 10

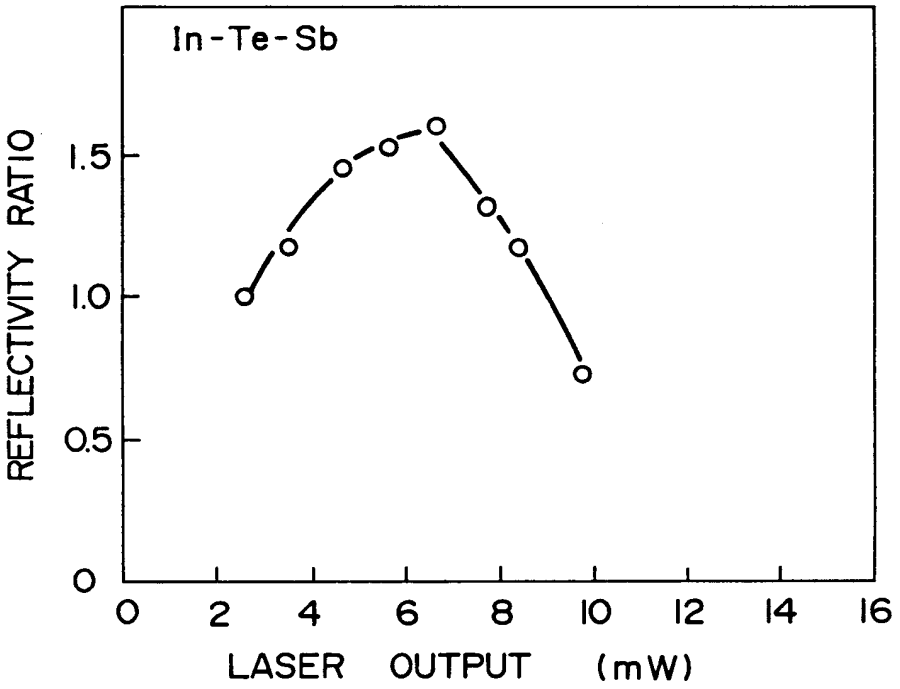

In-Te-Sb
REFLECTIVITY RATIO
1.5
1.0
0.5
0
0
2
4
6
8
10
12
14
16
LASER OUTPUT (mW)

FIG. 11a

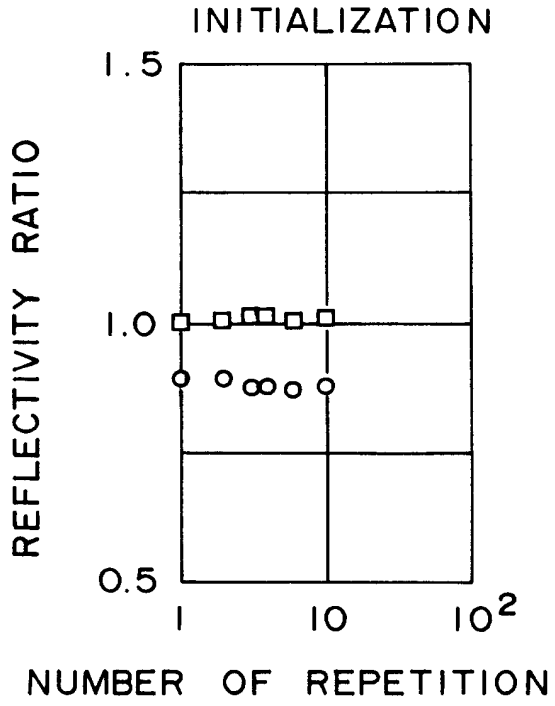


FIG. 11b

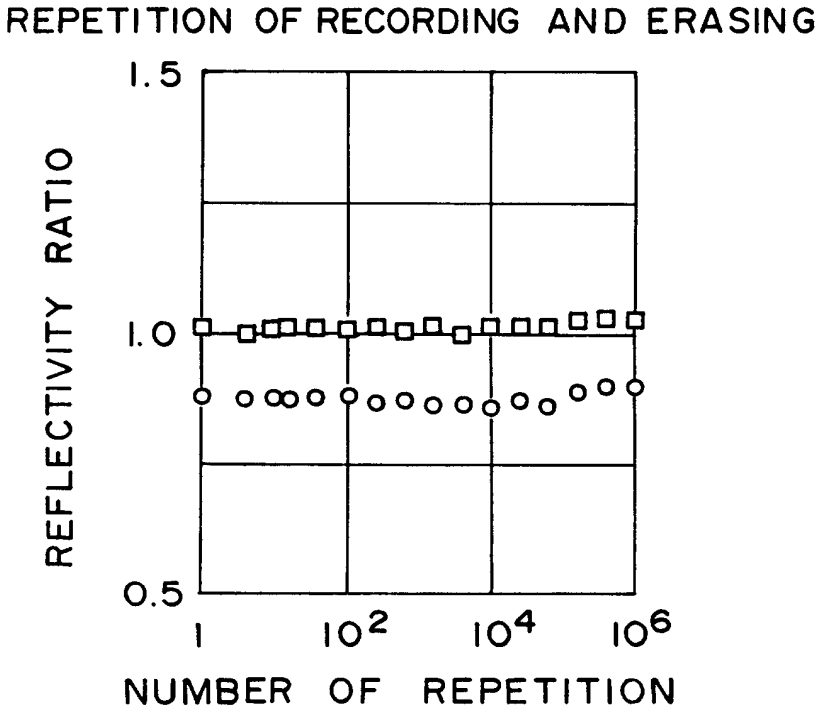


FIG. 12

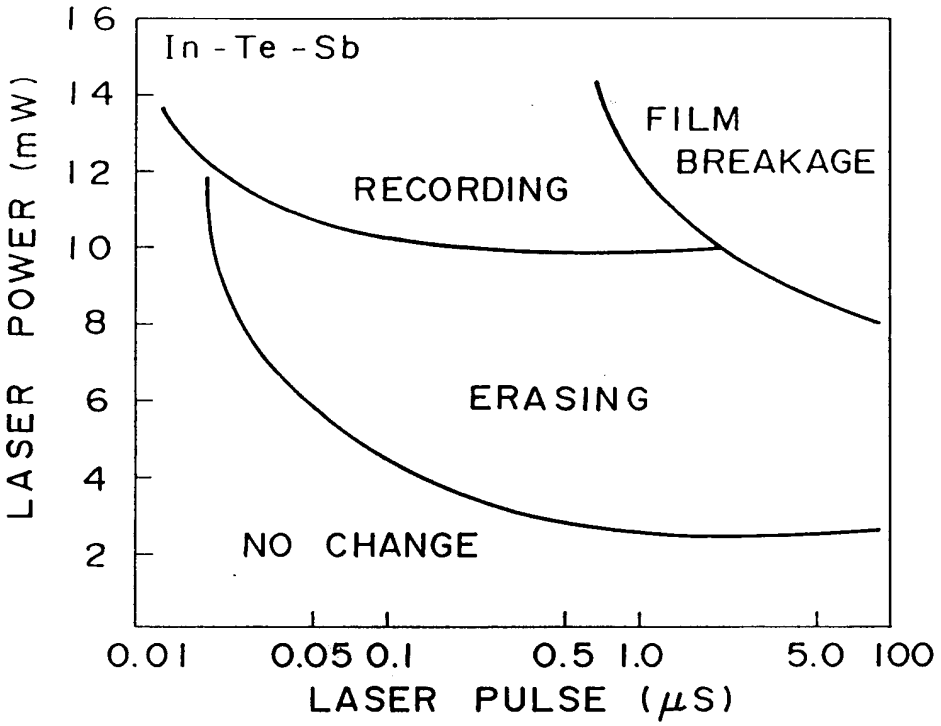

In - Te - Sb
FILM
BREAKAGE
RECORDING
ERASING
NO CHANGE
LASER POWER (mW)
16
14
12
10
8
6
4
2
0.01
0.05
0.1
0.5
1.0
5.0
100
LASER PULSE (μS)

FIG. 13

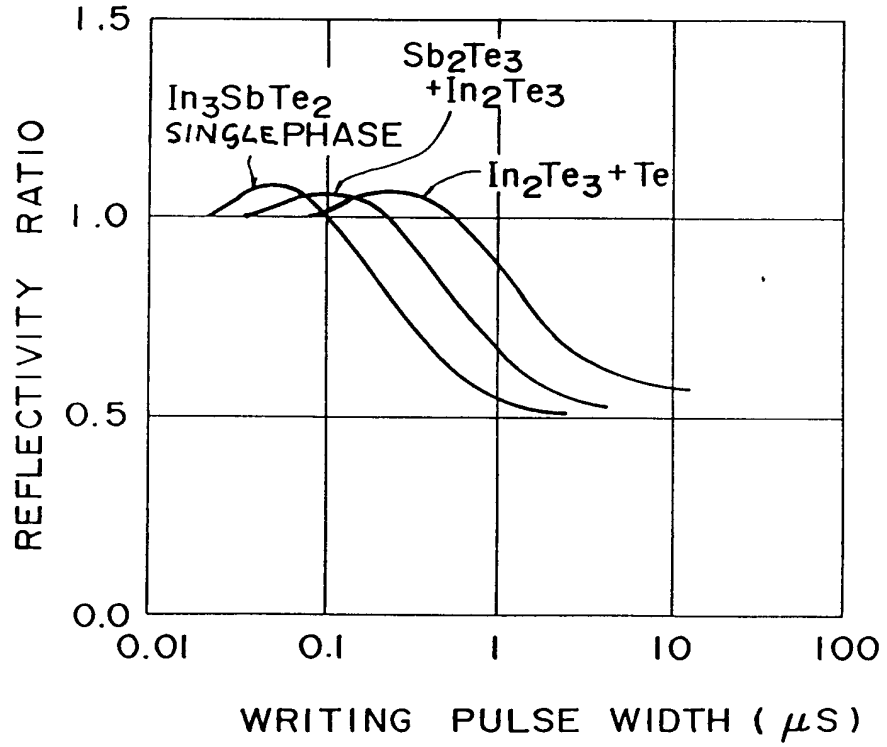

Sb2Te3
+In2Te3
In3SbTe2
SINGLEPHASE
In2Te3+Te
REFLECTIVITY RATIO
1.5
1.0
0.5
0.0
0.01
0.1
1
10
100
WRITING PULSE WIDTH (μS)

FIG. 14

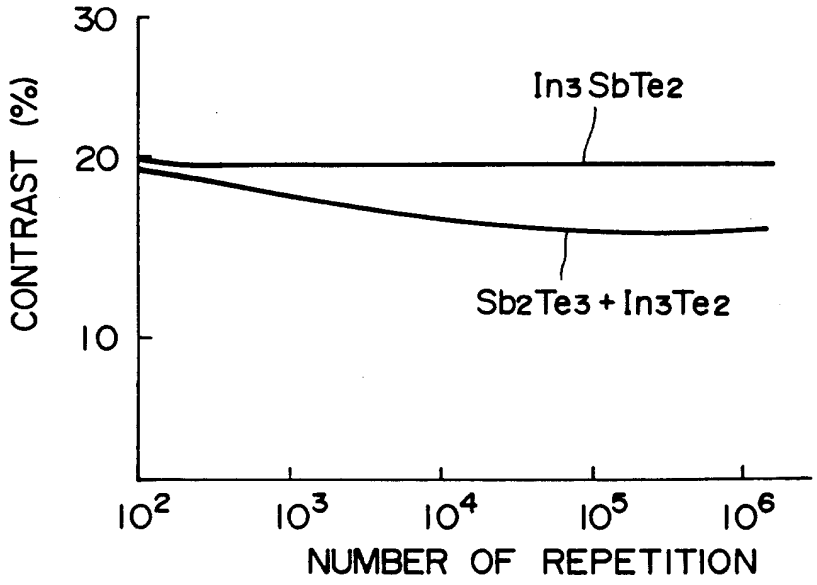

30
20
10
CONTRAST (%)
In3SbTe2
Sb2Te3 + In3Te2
10^2
10^3
10^4
10^5
10^6
NUMBER OF REPETITION

FIG. 15

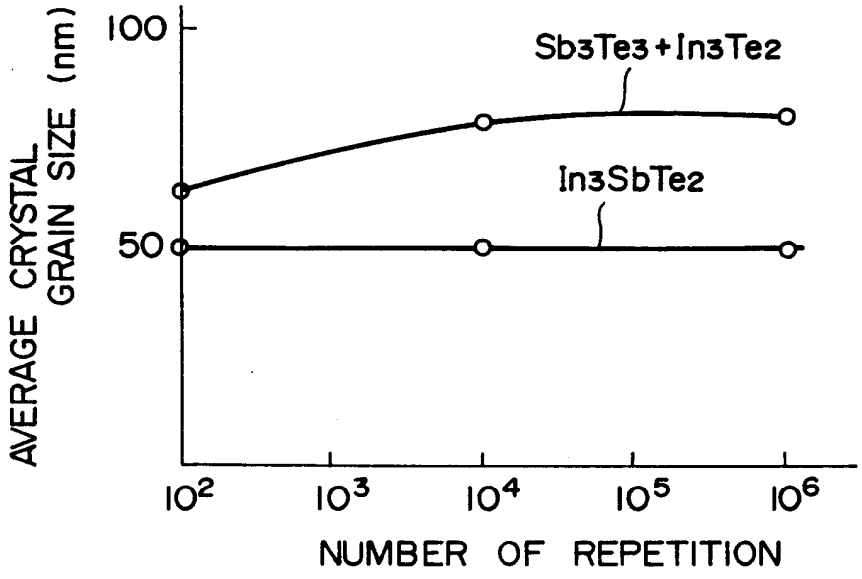

100
50
AVERAGE CRYSTAL GRAIN SIZE (nm)
Sb3Te3 + In3Te2
In3SbTe2
10^2
10^3
10^4
10^5
10^6
NUMBER OF REPETITION

FIG. 16

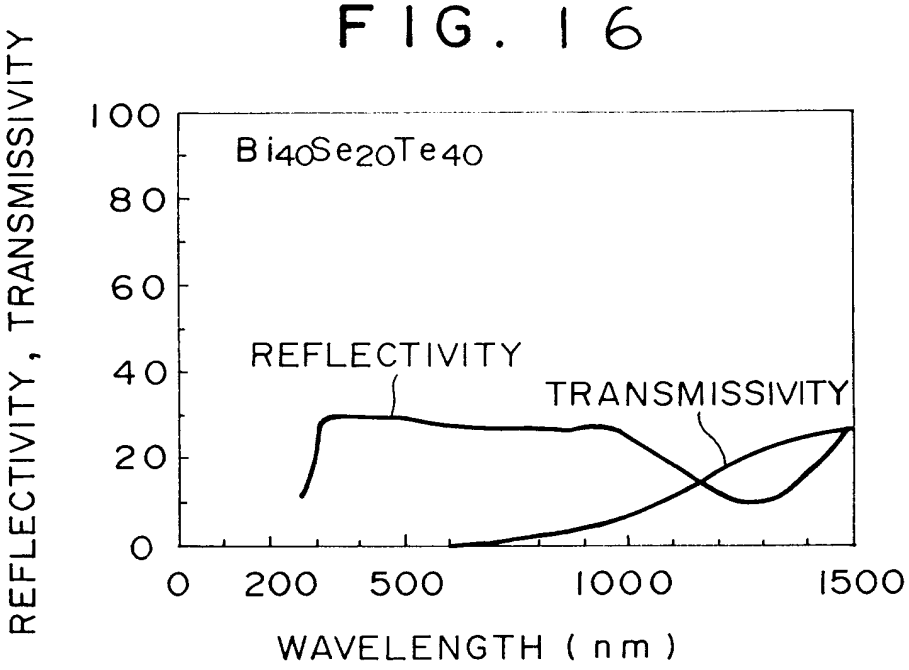

REFLECTIVITY, TRANSMISSIVITY
100
80
60
40
20
0
Bi40Se20Te40
REFLECTIVITY
TRANSMISSIVITY
0
200
500
1000
1500
WAVELENGTH (nm)

FIG. 17

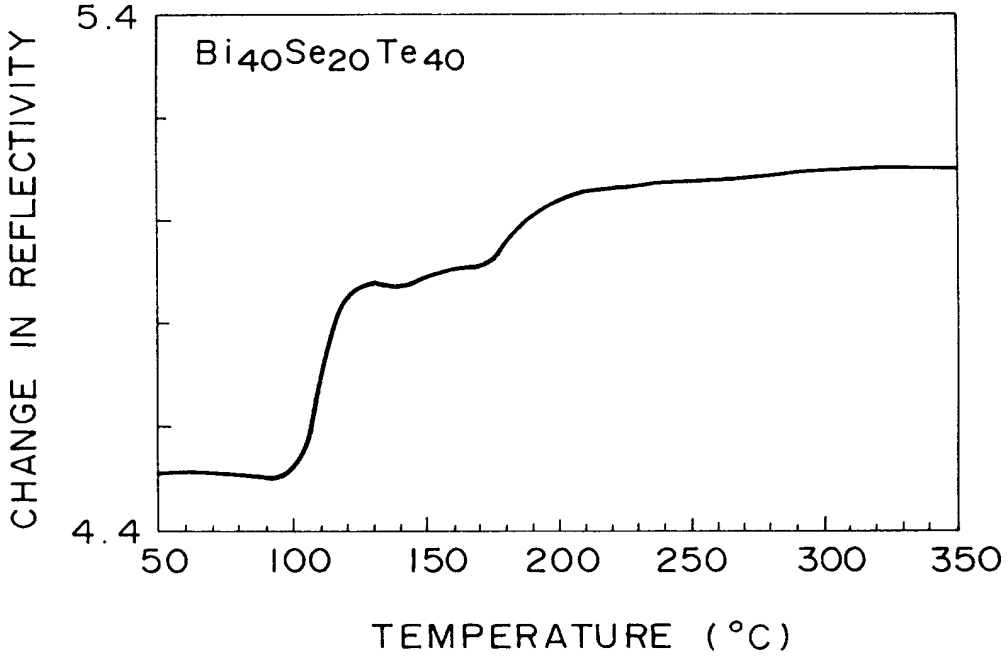

CHANGE IN REFLECTIVITY
5.4
4.4
Bi40Se20Te40
50
100
150
200
250
300
350
TEMPERATURE (°C)

FIG. 18

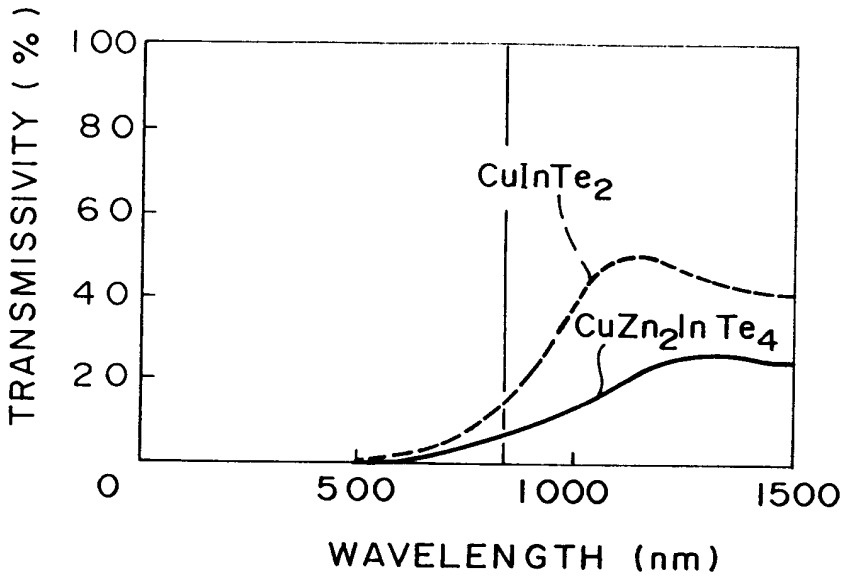

TRANSMISSIVITY (%)
100
80
60
40
20
0
500
1000
1500
WAVELENGTH (nm)
CuInTe2
CuZn2InTe4

FIG. 19

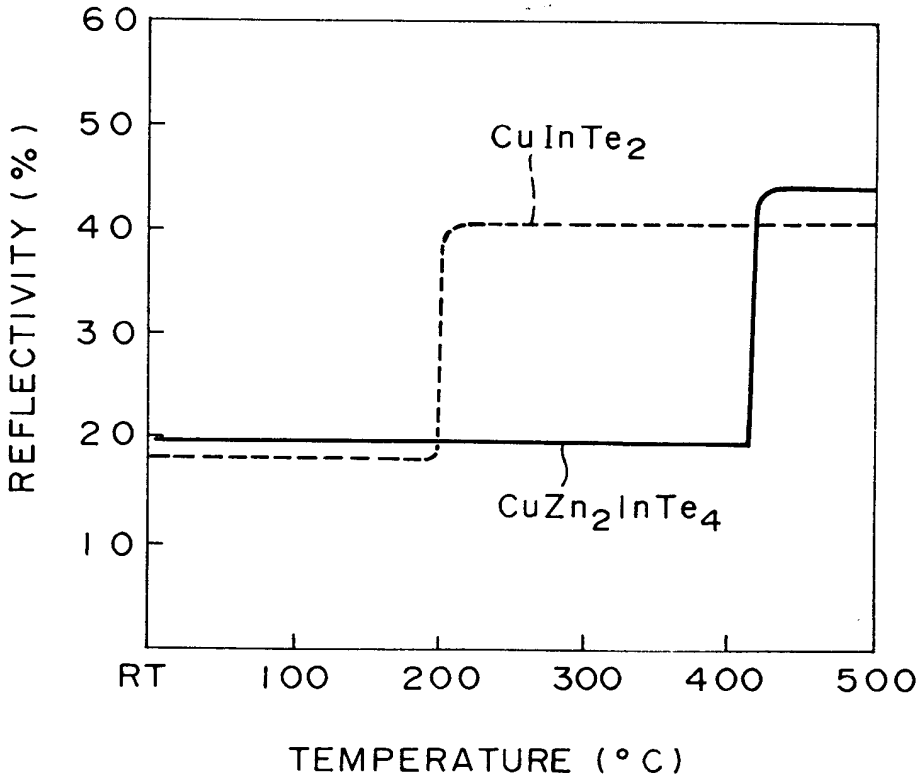

REFLECTIVITY (%)
60
50
40
30
20
10
RT
100
200
300
400
500
TEMPERATURE (°C)
CuInTe2
CuZn2InTe4

FIG. 20

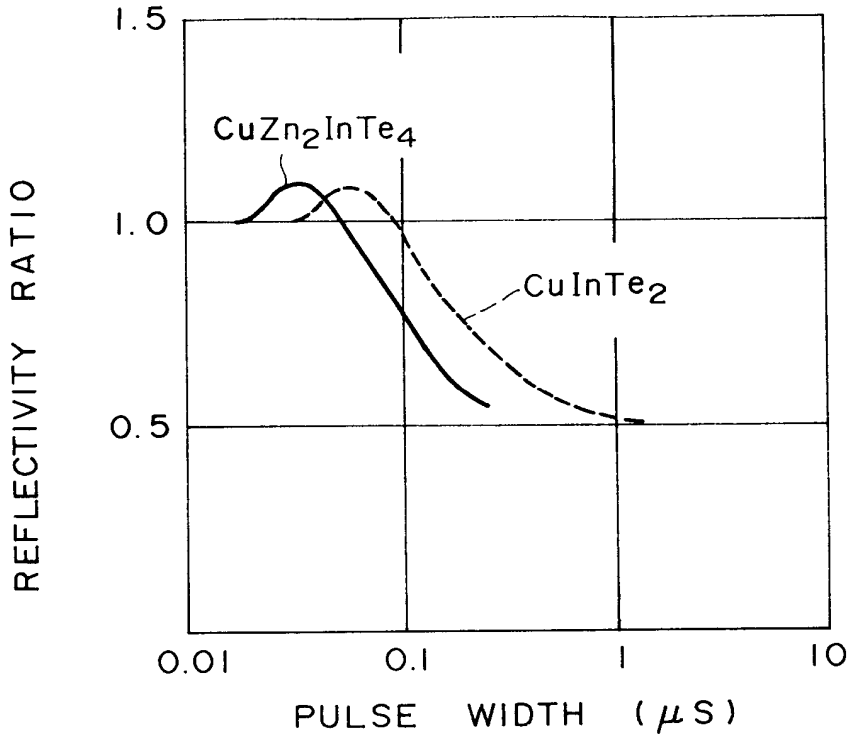

1.5
1.0
0.5
REFLECTIVITY RATIO
$CuZn_2InTe_4$
$CuInTe_2$
0.01
0.1
1
10
PULSE WIDTH (μS)

FIG. 21

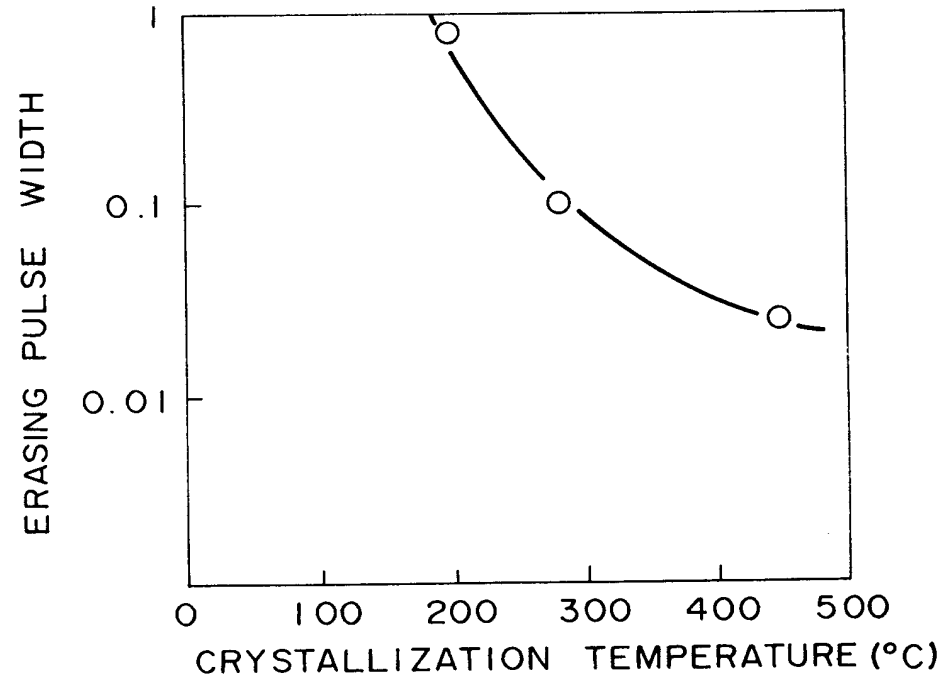
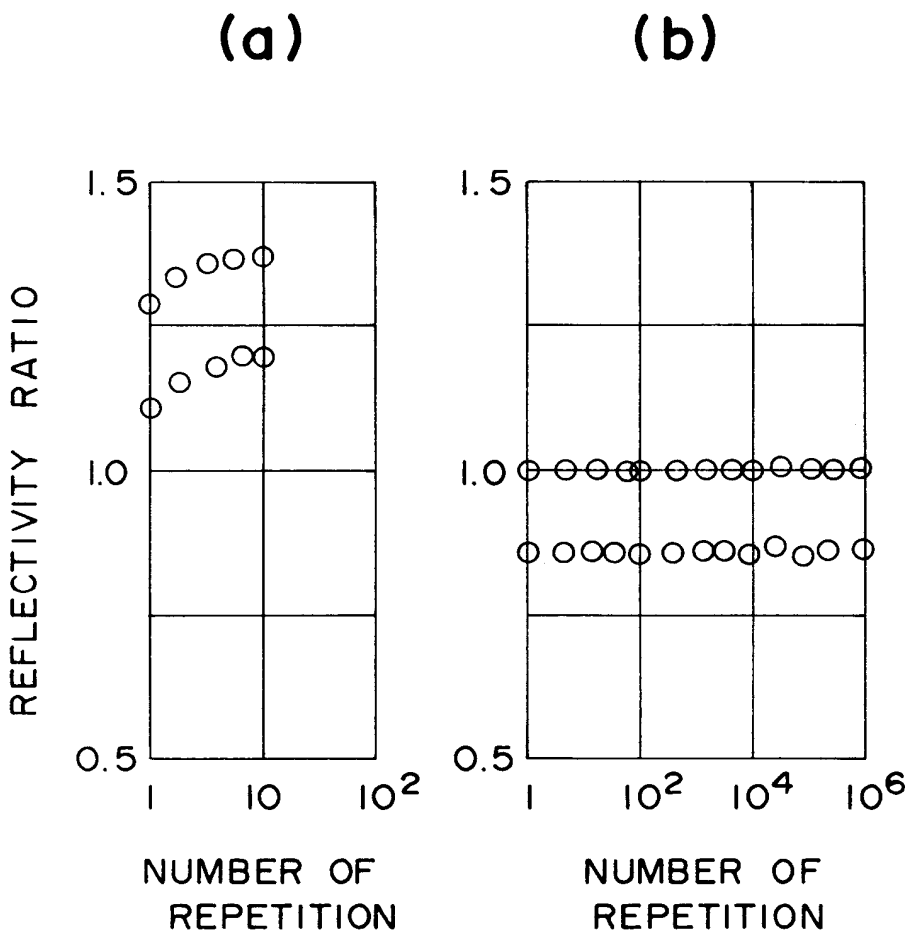

1
0.1
0.01
ERASING PULSE WIDTH
0
100
200
300
400
500
CRYSTALLIZATION TEMPERATURE (°C)

FIG. 22


(a)
(b)
1.5
1.0
0.5
REFLECTIVITY RATIO
1
10
10^2
NUMBER OF REPETITION
1
10^2
10^4
10^6
NUMBER OF REPETITION